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# Final Report on Thermal Problems in Material Processing of High-Temperature Materials

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## Abstract

In the annual reports other aspects of materials processing of high temperature materials, such as Heat Transfer in Fiber Formation, have been discussed. In this Final Report Axial Segregation in Unsteady Diffusion Dominated Directional Solidification of a Binary Alloy with a Planar Solid-Liquid Interface Profile is considered. The analysis is an extension of the work of Smith et al. [1] to account for an arbitrary initial axial concentration profile. This situation is important in the experimental studies of growth of crystals in a microgravity environment in which the growth is from melts formed by re-melting crystals that have a known axial impurity profile. Three situations are discussed. These are the initial transient, a re-solidified crystal, and multipass solidification.

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# 1 Introduction

In this article axial segregation in unsteady diffusion dominated solidification of a binary alloy is considered when an *arbitrary* initial concentration profile is given. It is an extension of the classical study of Smith et al. [1] who give the solution for dopant concentration distributions during initial and final transients in crystals grown from melts in which impurity distribution is initially *uniform*. The analysis should be of general interest to crystal growers, but the particular needs of experimenters who carry out crystal growing experiments in a microgravity environment were kept in mind. In their experiments crystals are grown from a melt that has been formed by re-melting a crystal that was grown by some method on earth. Hence the initial axial impurity distribution in the melt is not uniform, but a specified function of the axial coordinate.

In order to carry out the analysis by analytical methods, a number of assumtions were made. The major ones include neglecting convection and changes in the volume as the material melts. The first is closely approximated in space, and the second is an assumed property of the material. In addition remelting between successive passes was assumed to be instantanous and thus diffusion in the melt was neglected during the remelting process. How well this can be achieved in practice depends on the furnace design and the smallness of the diffusion coefficient. The final transient was also ignored, since it contributes only to the local concentration in the far end of the ampoule. The influence of phase boundary curvature was neglected in this study. Its influence under steady growth has been most recently reported by Korpela et al. [2].

From the above list, it is clear that in order to carry the analytical study a number of assuptions are needed, assumptions which could have been relaxed, in a purely computational study. The advantage of carrying the analysis analytically is the possibility of obtaining explicit solutions which are easily programmed and from which special results for various materials can be gleaned. It is with this aim that this study was undertaken.

# 2 Formulation

Consider the directional solidification of a melt in an infinite cylindrical ampoule. The periphery is insulated and impermeable, and the temperatures of the ends are such that solidification takes place. The origin of coordinates is fixed to the mean position of the solidification front. If the coordinates move with the solidification rate, in these coordinates the solidification front is stationary and the melt moves toward it at a constant speed $V$.

For semiconductors the coefficient of mass diffusion $D$ in the solid is several orders of magnitude smaller than it is in the fluid phase. Thus solute diffusion in the solid can be ignored. By introducing the non-dimensional variables

$$x = \frac{Vx'}{D} \qquad t = \frac{V^2 t'}{D} \qquad C = \frac{C'}{C_o} \tag{1}$$

the concentration field of the solute is governed by

$$\frac{\partial C}{\partial t} - \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial x^2} \tag{2}$$

and initial, boundary, and interface conditions are

$$C(x,0) = f(x), \qquad C(\infty,t) = 1, \qquad \frac{\partial C}{\partial x}(0,t) + (1-k)C(0,t) = 0 \tag{3}$$

where the distribution coefficient $k = C_s(0)/C(0,t)$ has been introduced. It is the ratio of the slopes of the liquidus and solidus lines in an ideal phase diagram in which these lines are taken to be straight. The initial condition $f(x)$ is a given function that tends to unity far from the solidification front.

# 3 Solution

The mathematical problem formed by Eqns. (2) and (3) for unsteady diffusion equation is solved by employing a Green's function, which satisfies

$$\frac{\partial G}{\partial t} - \frac{\partial G}{\partial x} = \frac{\partial^2 G}{\partial x^2} \tag{4}$$

$$G(x,0) = \delta(x-\xi), \qquad \frac{\partial G}{\partial x}(0,t) + (1-k)G(0,t) = 0, \qquad G(\infty,t) = 0 \tag{5}$$

The solution obtained by Laplace transform technique. The Green's function is

$$G(x|\xi,t) = \left(\frac{1}{2} - k\right) e^{-(1-k)(x+kt)+k\xi} \operatorname{erfc}\left[\frac{x-\xi}{2\sqrt{t}} - \left(\frac{1}{2}-k\right)\sqrt{t}\right]$$

$$+\frac{1}{2\sqrt{\pi t}} e^{-\frac{1}{2}(x-\xi)-\frac{t}{4}} \left[e^{-\frac{(x+\xi)^2}{4t}} + e^{-\frac{(x-\xi)^2}{4t}}\right] \tag{6}$$

Although the operator for the Green's function is not self-adjoint, the solution for the concentration field can be expressed, as shown in Stakgold [3], in term of the original Green's function by proper identification of the variables $x$ and $\xi$. Details of the solution method are given in Kim [4].

In terms of the Green's function the concentration field can be written as

$$C(x,t) = \int_0^\infty G(x|\xi,t) f(\xi) d\xi \tag{7}$$

This is a convenient form not only for obtaining analytical solutions for simple initial concentration fields, but also for numerical evaluation for quite general initial distributions $f(x)$.

# 4 Results

## 4.1 Initial Transient

When the initial melt is uniform in composition so that $f(x) = 1$. integration of the Green's function gives

$$C(x,t) = \int_0^\infty G(x|\xi,t)d\xi = \frac{1-k}{2k}e^{-x}\mathrm{erfc}[\frac{1}{2\sqrt{t}}(x-t)] - \frac{1}{2}\mathrm{erfc}[\frac{1}{2\sqrt{t}}(x+t)]$$
$$-\frac{1-2k}{2k}e^{-(1-k)(x+kt)}\mathrm{erfc}[\frac{1}{2\sqrt{t}}(x-(1-2k)t)] \quad (8)$$

This result is not new, for it was first obtained by Smith et al. [1]. It is given here as a special case of Eqn. (7). In dimensional variables the concentration distribution is

$$\frac{C'(x',t')}{C_o} = 1 + \frac{1-k}{2k}e^{-Vx'/D}\mathrm{erfc}[\frac{1}{2\sqrt{Dt'}}(x'-Vt')] - \frac{1}{2}\mathrm{erfc}[\frac{1}{2\sqrt{Dt'}}(x'+Vt')]$$
$$-\frac{1-2k}{2k}e^{-(1-k)(Vx'/D+kV^2t'/D)}\mathrm{erfc}[\frac{1}{2\sqrt{Dt'}}(x'-(1-2k)Vt')] \quad (9)$$

The concentration at $x' = Vt'$ multiplied by $k$ is frozen into the crystal because $D_s/D \ll 1$. Thus the impurity concentration in the crystal in dimensional terms, obtained by putting $x' = 0$ and then setting $t' = x'/V$, is

$$C_s(x') = kC(0,t') = \frac{C_o}{2}\left[[1+\mathrm{erf}(\sqrt{\frac{Vx'}{4D}})] + (2k-1)e^{-(1-k)kVx'/D}\mathrm{erfc}[(2k-1)\sqrt{\frac{Vx'}{4D}}]\right] \quad (10)$$

This result for $C_s$ is shown in Figure 1 for various values of $k$, and it is the same as that first given by Smith et al. [1]. It is repeated here for the sake of completeness.

## 4.2 Re-melting and Solidification

In space experiments crystals are grown by re-solidifying a melt that has been formed from re-melted crystals. Hence for them the initial condition $f(x) = C_s(x)$ is that obtained from the initial transient solution (10), which in dimensionless terms is

$$f(x) = \frac{1}{2}\left[[1+\mathrm{erf}(\sqrt{\frac{x}{4}})] + (2k-1)e^{-(1-k)kx}\mathrm{erfc}[(2k-1)\sqrt{\frac{x}{4}}]\right] \quad (11)$$

The concentration in the re-solidified crystal is given by Eqn. (7) with this as the initial condition. Thus the impurity concentration in the crystal can be expressed as

$$C_s(t) = kC(0,t) = \frac{k}{2}\int_0^\infty \left[(\frac{1}{2}-k)e^{-(1-k)kt+k\xi}\,\mathrm{erfc}[\frac{\xi}{2\sqrt{t}} - (\frac{1}{2}-k)\sqrt{t}] + \frac{1}{\sqrt{\pi t}}e^{\frac{\xi}{2}-\frac{t}{4}-\frac{\xi^2}{4t}}\right]$$

$$\left[[1+\mathrm{erf}(\sqrt{\frac{\xi}{4}})]+(2k-1)e^{-(1-k)k\xi}\ \mathrm{erfc}[(2k-1)\sqrt{\frac{\xi}{4}}]\right]d\xi \tag{12}$$

The axial distribution in the solidified crystal is now obtained by simply replacing $t$ by $x$ in this expression and it is given by

$$C_s(x)=\frac{k}{2}\int_0^\infty\left[(\frac{1}{2}-k)e^{-(1-k)kx+k\xi}\ \mathrm{erfc}[\frac{\xi}{2\sqrt{x}}-(\frac{1}{2}-k)\sqrt{x}]+\frac{1}{\sqrt{\pi x}}e^{\frac{\xi}{2}-\frac{x}{4}-\frac{\xi^2}{4x}}\right]$$

$$\left[[1+\mathrm{erf}(\sqrt{\frac{\xi}{4}})]+(2k-1)e^{-(1-k)k\xi}\ \mathrm{erfc}[(2k-1)\sqrt{\frac{\xi}{4}}]\right]d\xi \tag{13}$$

The solution is in the form of a quadrature and is plotted in Figure 2 for different values of $k$.

If $k=1/2$, the solution simplifies greatly for three of the terms making up the integrand vanish and the remaining terms can be integrated in closed form. By splitting the integral in

$$C_s(x)=\frac{e^{-\frac{x}{4}}}{4\sqrt{\pi x}}\int_0^\infty e^{\frac{\xi}{2}-\frac{\xi^2}{4x}}\left[1+\mathrm{erf}(\sqrt{\frac{\xi}{4}})\right]d\xi \tag{14}$$

into two parts, the first one is

$$\int_0^\infty e^{\frac{\xi}{2}-\frac{\xi^2}{4x}}d\xi=\sqrt{\pi x}\ e^{\frac{x}{4}}\left[1+\ \mathrm{erf}(\sqrt{\frac{x}{4}})\right] \tag{15}$$

To evaluate the second, the error function is represented by its series

$$\mathrm{erf}(z)=\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n+1}}{n!(2n+1)} \tag{16}$$

and a term by term integration is carried out. This yields

$$\int_0^\infty e^{\frac{\xi}{2}-\frac{\xi^2}{4x}}\ \mathrm{erf}(\sqrt{\frac{\xi}{4}})d\xi=\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n}{2^{2n+1}n!(2n+1)}\int_0^\infty e^{\frac{\xi}{2}-\frac{\xi^2}{4x}}\ \xi^{n+\frac{1}{2}}d\xi \tag{17}$$

The integral on the right can be written as

$$\int_0^\infty e^{\frac{\xi}{2}-\frac{\xi^2}{4x}}\ \xi^{n+\frac{1}{2}}d\xi=x^{\frac{n}{2}+\frac{1}{4}}\ \Gamma(n+\frac{3}{2})U(\frac{n}{2}+\frac{3}{4};\frac{1}{2};\frac{x}{4}) \tag{18}$$

and $U(a;b;c)$ is the confluent hypergeometric function of the second kind [5].

The concentration distribution in the crystal can thus be written as

$$C_s(x)=\frac{1}{4}\left[1+\ \mathrm{erf}(\sqrt{\frac{t}{4}})\right]+\frac{e^{-\frac{x}{4}}}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n x^{\frac{1}{2}(n+\frac{1}{2})}}{2^{2n+2}(2n+1)n!}\ \Gamma(n+\frac{3}{2})U(\frac{n}{2}+\frac{3}{4};\frac{1}{2};\frac{x}{4}) \tag{19}$$

or in dimensional terms as

$$\frac{C_s'(x')}{C_o} = \frac{1}{4}\left[1+\mathrm{erf}(\sqrt{\frac{Vx'}{4D}})\right] + \frac{e^{-\frac{Vx'}{4D}}}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n(\frac{Vx'}{D})^{\frac{1}{2}(n+\frac{1}{2})}}{2^{2n+2}(2n+1)n!}\Gamma(n+\frac{3}{2})U(\frac{n}{2}+\frac{3}{4};\frac{1}{2};\frac{Vx'}{4D}) \quad (20)$$

This solution is plotted in Figure 3 and it together with Figures 1 and 2 shows the effect of a second pass on the reduction of the impurity concentration.

## 4.3 Multipass Solidification

Often in industrial practice there is a need to purify crystals by zone refinement. Although only a region of finite length is remelted, the theory in this section serves as a qualitative guide to the purification achieved by multiple meltings and subsequent solidifications.

After the first pass concentration in the solid can be written as

$$C_s(x) = \int_0^\infty G(0|\xi,x)f(\xi)d\xi. \quad (21)$$

Since the initial condition $f(\xi)$ is the previous solid concentration, for the $n$-th pass the concentration can be expressed as

$$C_s^{(n)}(x) = \int_0^\infty G(0|\xi,x)C_s^{(n-1)}(\xi)d\xi. \quad (22)$$

Evaluating the integral numerically gives

$$C_s^{(n)}(x_i) = \sum_{j=1}^{m} G(0|\xi_j,x_i)C_s^{(n-1)}(\xi_j)w_j, \quad (23)$$

where $w_j$'s are the weigths of a given quadrature rule. In matrix notation this can be written as

$$C_{si}^{(n)} = A_{ij}C_{sj}^{(n-1)} \quad (24)$$

where the matrix elements are $A_{ij} = G_{ij}\cdot w_j$ (no summation convention on indices is implied here). Using this result recursively gives

$$C_{si}^{(n)} = A_{ij}^n C_{sj}^{(0)} \quad (25)$$

where $C_{sj}^{(0)}$ is the initial concentration distribution. This is a handy formula, which allows the concentration for the $n$-th pass of solidification to be obtained directly by matrix multiplications. Wide availability of computational tools, such as MATLAB, for matrix calculations makes generation of results particularly simple. The results shown in Figure 4 are for up to 50 re-solidifications.

# 5 Conclusions

By finding the Green's function for unsteady concentration equation, analytical results were obtained for the concentration distribution in a crystal, which initially has a uniform impurity distribution, and for the distribution in a re-solidified crystal, with an initial concentration distribution set by the first pass. This advances the theory over that worked out by Smith et al. [1] by allowing arbitrary initial conditions to be considered. The results will serve the needs of experimentalists who carry out experiments in a micro-gravity environment. Since the solution (7) is in terms of a Green's function, the $n$-th pass of re-solidification can be evaluated by numerical integration and a few matrix multiplications. This makes the analysis of multiple passes particularly simple to program and thus useful to practitioners.

# 6 Acknowledgments

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# List of Symbols

| Symbol | Representation |
|---|---|
| $C$ | concentration of impurity |
| $C_0$ | concentration of impurity in the far field |
| $D$ | diffusion coefficient |
| $G$ | Green's function |
| $k$ | partition coefficient |
| $t$ | time |
| $U$ | confluent hypergeometric function |
| $V$ | velocity |
| $x$ | spatial coordinate |
| $\Gamma$ | Gamma function |
| $\xi$ | location of delta function |

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Fig. 3. Effect of re-solidification on impurity concentration of crystal for $k = 0.5$.
Fig. 4. Effect of number of solidification on impurity concentration of crystal for $k = 0.5$.

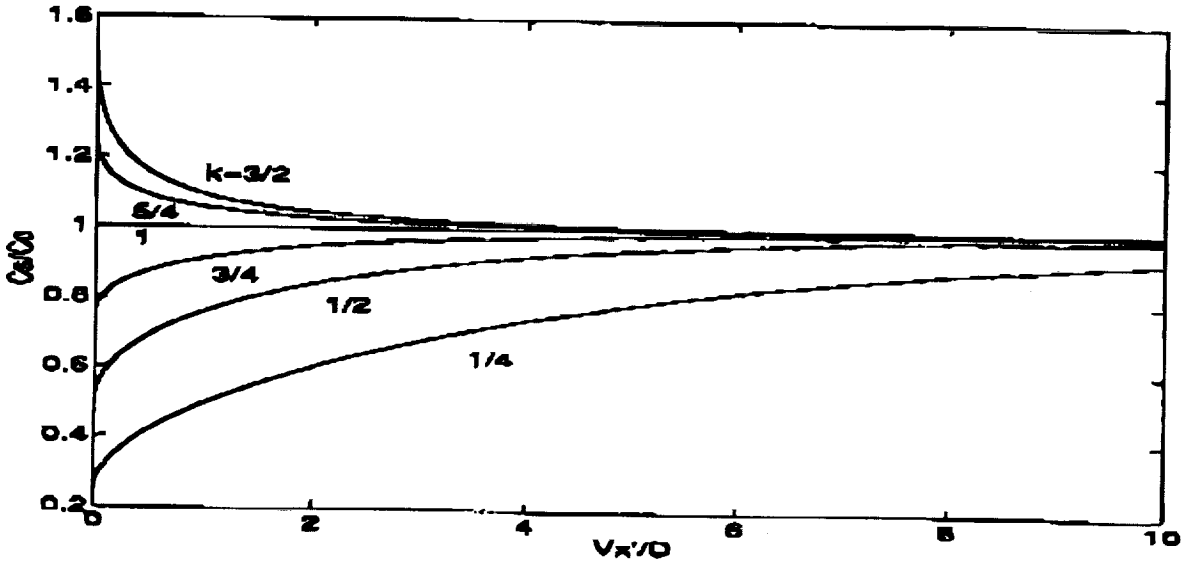


**Figure 1: The influence of the initial transient on the axial impurity concentration for various values of $k$.**

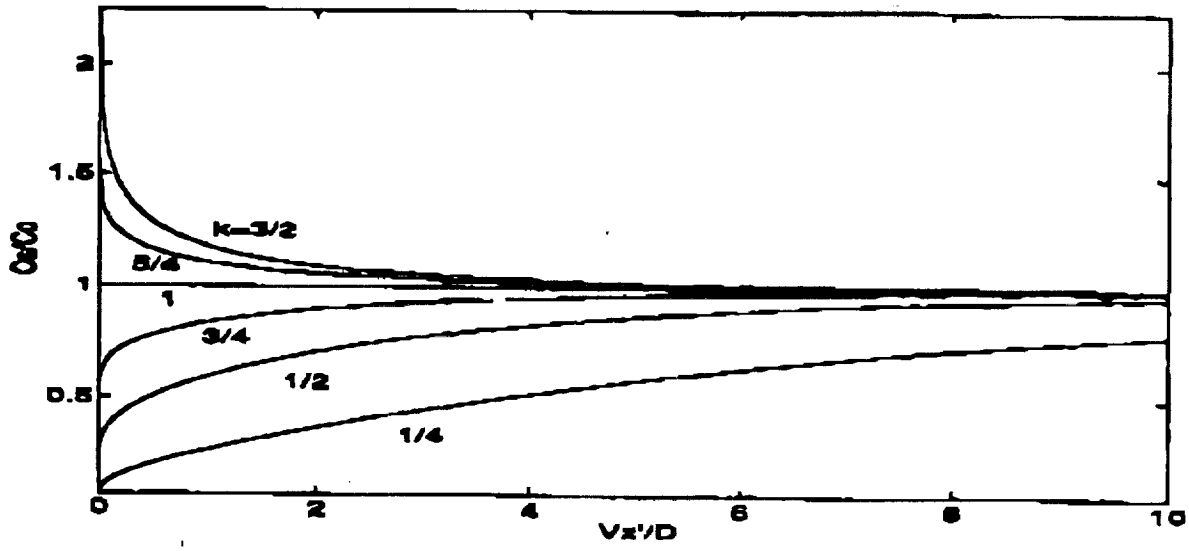


Figure 2: Axial impurity concentration after re-solidification for various values of $k$.

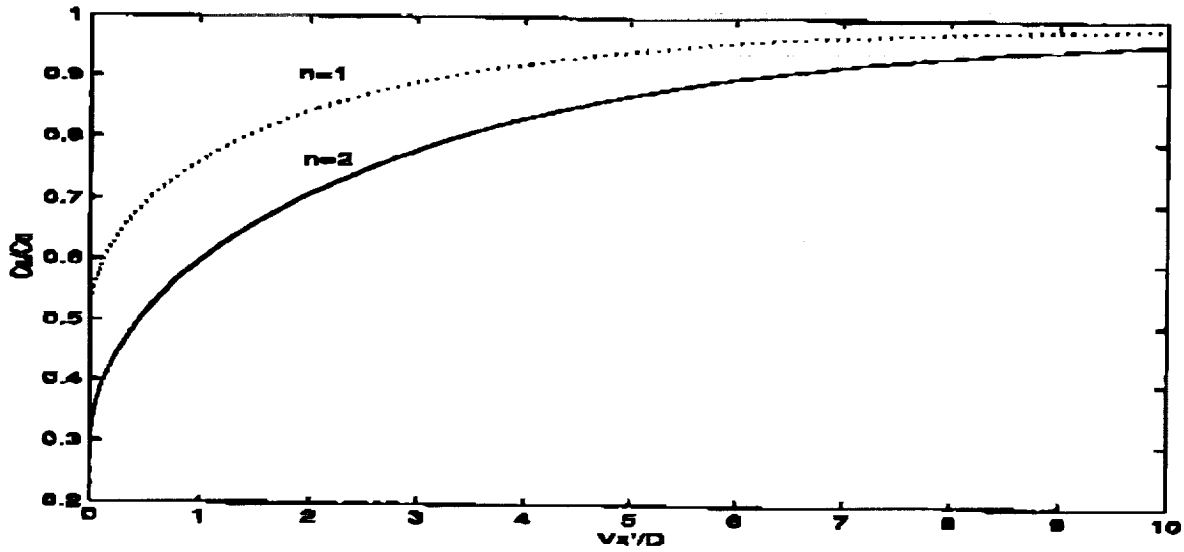


Figure 3: Effect of re-solidification on impurity concentration for a crystal with $k = 0.5$.

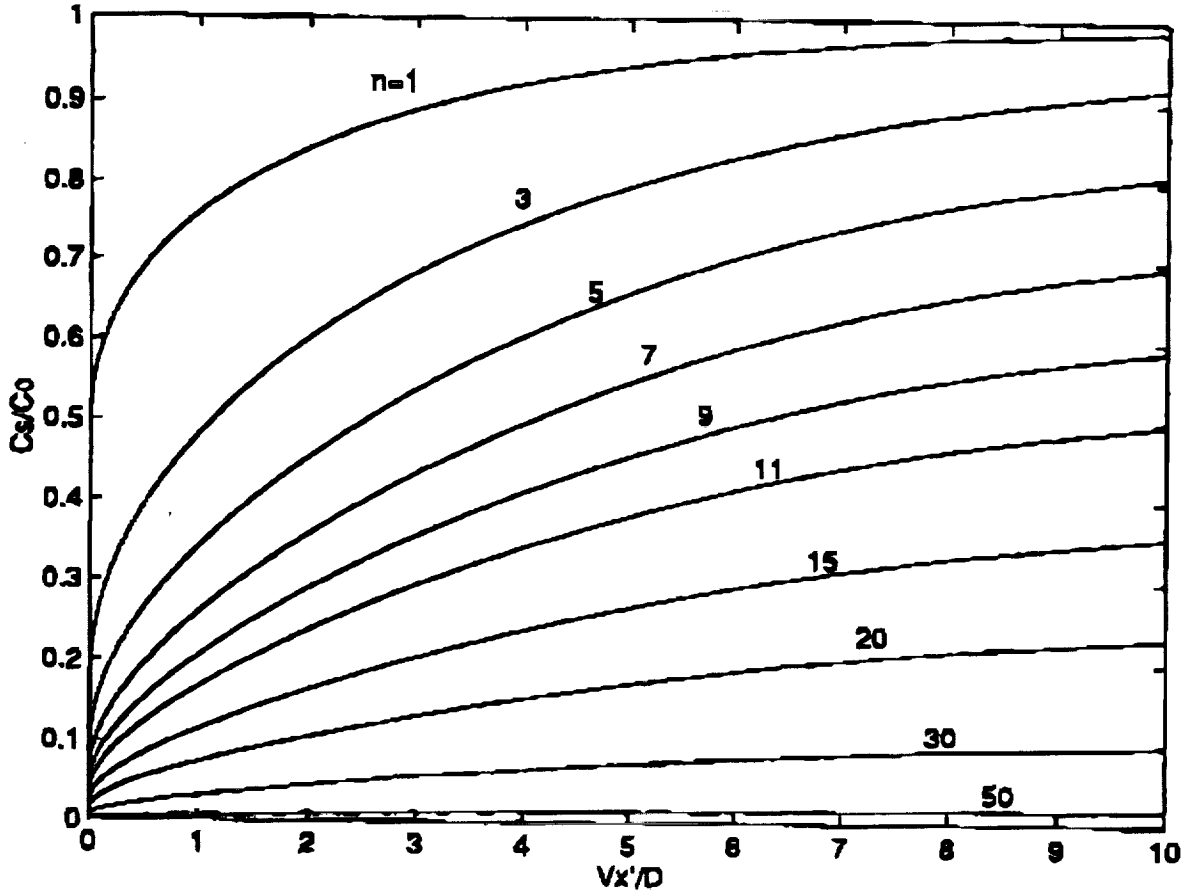


**Figure 4:** Effect of the number of solidification passes on impurity concentration of a crystal with $k = 0.5$.